

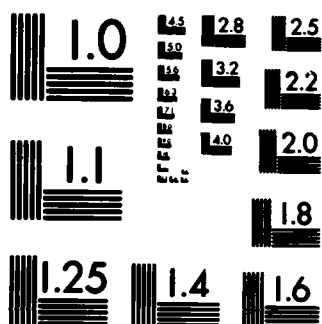
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TRIVALENT ION EXCHANGE IN BETA" ALUMINA

by

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Prepared for Publication

in

Solid State Ionics

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# TRIVALENT ION EXCHANGE IN BETA" ALUMINA

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## ABSTRACT

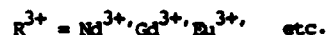
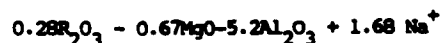
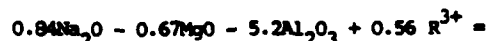
Ion exchange techniques were used to substitute trivalent cations for the sodium ions present in sodium beta" alumina single crystals. Complete replacement was achieved using  $Gd^{3+}$ ,  $Nd^{3+}$ , and  $Eu^{3+}$  ions in molten salts. The conductivity of  $Gd^{3+}$  beta" alumina was measured and optical properties of  $Nd^{3+}$  exchanged materials were studied. The trivalent beta" aluminas appear to be the first solid electrolytes to exhibit rapid trivalent cation motion at moderate temperatures.

## 1. Introduction

In our previous ion exchange studies we found that the entire sodium ion content of beta" alumina could be replaced by various divalent cations [1]. These studies indicate that the range of divalent beta" alumina compositions is quite broad and that the resulting compounds are a new family of high conductivity solid electrolytes for divalent cations. Furthermore, these divalent materials demonstrate that the phenomenon of fast ion transport in solids is not restricted to selected monovalent ions. Our recent experiments extend this observation. We have found that the beta" aluminas are capable of supporting trivalent cation motion. Several different trivalent cations have been exchanged for sodium in beta" alumina and in three cases we have synthesized completely exchanged (or nearly so) trivalent beta" alumina compositions. The preparation of these materials and preliminary measurements of their properties are reported in this paper.

## 2. Preparation of Trivalent Beta" Aluminas

The trivalent beta" alumina compositions were prepared by the ion exchange of single crystals of Na" beta" alumina. Specific experimental procedures were similar to those described for the divalent beta" aluminas [1]. Careful atmosphere control was required in order to remove water from the halide salts and to minimize the formation of refractory oxyhalide compounds during melting. The conditions used for trivalent ion exchange are summarized in Table 1. The extent of exchange was determined by radiochemical and/or weight change methods. In the latter case the weight increase was consistent with the exchange reaction



Results show that substantial exchange occurred for all of the trivalent ions and that complete exchange (or within 5%) was found for  $Gd^{3+}$ ,  $Nd^{3+}$  and  $Eu^{3+}$ . The greater melting points of the trivalent halide salts required higher synthesis temperatures than were used for the divalent materials. Nevertheless, considerable ion exchange was observed in the 600°C range when lower melting salts were available ( $GdCl_3$ ) or when eutectic melt compositions ( $PrCl_3$  -  $NaCl$ ,  $NdCl_3$  -  $NaCl$ ) were employed. In addition, the large amount of exchange with  $BiCl_3$  at 270°C is a strong indication of rapid trivalent ion diffusion in the beta" aluminas. In contrast to the results in Table 1, single crystals of sodium beta alumina immersed in the  $PrCl_3$  -  $NaCl$  melt for 54 hours produced no measurable exchange. The very different response of beta and beta" alumina to multivalent ion transport was discussed previously. [1]

The trivalent exchanged crystals were found to be in good condition with no evidence of cracking. The crystals remained transparent although  $Nd^{3+}$  exchanged samples exhibited a slight blue tint. X-ray diffraction analysis confirmed that the beta" alumina structure was retained, however, the  $Tb^{3+}$  material appeared to possess some subtle structural modification. The exact nature of this change was not identified.

Table 1  
Trivalent Ion Exchange Conditions

ion	Melt Composition	Temp (°C)	time(h)	%exchange
Gd <sup>3+</sup>	GdCl <sub>3</sub>	615	5	100
Nd <sup>3+</sup>	NdBr <sub>3</sub>	720	0.5	95
Nd <sup>3+</sup>	45 NdCl <sub>3</sub> /55 NaCl	600	12	53
Eu <sup>3+</sup>	EuCl <sub>3</sub>	870	20	95
Yb <sup>3+</sup>	YbCl <sub>3</sub>	740	24	90
Sm <sup>3+</sup>	SmCl <sub>3</sub>	700	20	90
Tb <sup>3+</sup>	TbCl <sub>3</sub>	740	48	90
Dy <sup>3+</sup>	DyCl <sub>3</sub>	1000	0.5	70
Bi <sup>3+</sup>	BiCl <sub>3</sub>	270	12	70
Pr <sup>3+</sup>	37 PrCl <sub>3</sub> /63 NaCl	600	54	43

### 3. Electrical and Optical Properties

The conductivity for Gd<sup>3+</sup> beta" alumina was measured by ac impedance techniques. Initial results are shown in Fig. 1 and compared to a typical divalent (Ba<sup>2+</sup>) and to Na beta" alumina. [2] The lower conductivity for Gd<sup>3+</sup> and the greater activation energy for conduction are expected because of the more difficult process of transporting an ion of higher charge within the conduction plane. The low conductivity at room temperature is consistent with the structure data which show Gd<sup>3+</sup> ions locked in bonds to column oxygen. [3] At higher temperatures, however, the trivalent ions are quite mobile. The conductivity at 400°C ( $\sim 8 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ ) concurs with the diffusion rate extrapolated from the ion exchanged treatments and is actually comparable to the conductivity of  $\sigma''$  in calcia stabilized zirconia.

The measured conductivity values are sufficiently low that they may be influenced by trace Na in the conduction plane. These possible contributions are not yet identified and require complementary transport measurements and accurate determination of residual Na<sup>+</sup> content. Nonetheless, the low temperature exchange of Bi<sup>3+</sup> and the ability to achieve complete replacement within the temperature and time periods of exchange provides corroborative evidence of fast trivalent cation motion. At this time, the trivalent beta" aluminas appear to be the first crystalline compounds to exhibit high conductivity for trivalent cations.

The rare earth ions exchanged into sodium beta" alumina are optically active and preliminary experiments indicate that all of these trivalent compositions fluoresce. This behavior suggests that the exchange of rare earth ions may be used as a very sensitive optical probe to determine local structure and ion distributions in the conduction plane. In this paper, some initial optical measurements on Nd<sup>3+</sup> beta" alumina are presented. A more thorough spectroscopy study of this material will be published elsewhere.

The fluorescence spectra of Nd<sup>3+</sup> exchanged beta" alumina are generally similar to that of Nd<sup>3+</sup> in Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG). The latter material is one of the most common and successful solid state laser hosts. The optical transitions and linewidths are virtually the same for both compositions, the only difference being that the spectra in beta" alumina are shifted to shorter wavelengths by approximately 10 nm. This shift arises from the different local structures of the two host materials.

The ability to rapidly and completely exchange Nd<sup>3+</sup> into beta" alumina has enabled us to investigate the fluorescence lifetime of the <sup>4</sup>F<sub>3/2</sub> state as a function of Nd<sup>3+</sup> concentration. Table 2 compares results for beta" alumina, YAG and La<sub>1-x</sub>Nd<sub>x</sub>MgAl<sub>11</sub>O<sub>19</sub> (LNA) host materials. LNA, an aluminate compound with the magnetoplumbite structure, is a candidate material for high power laser applications. [5] The values shown

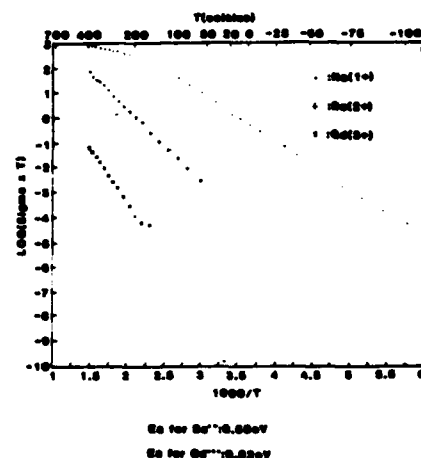


Fig. 1 Conductivity of monovalent (Na<sup>+</sup>), divalent (Ba<sup>2+</sup>) and trivalent (Gd<sup>3+</sup>) beta" alumina single crystals

Table 2

Fluorescence Lifetime for  $\text{Nd}^{3+}$  in Various Host Materials

Host Material	$\text{Nd}^{3+}$ Concentration ( $\text{cm}^{-3}$ )	Fluorescence Lifetime ( $\mu\text{s}$ )	Ref.
Beta" Alumina	$4.0 \times 10^{19}$	395	This Work
	$8.5 \times 10^{20}$	350	This Work
	$1.5 \times 10^{21}$	350	This Work
$\text{Y}_3\text{Al}_5\text{O}_{12}$	ca. $1.4 \times 10^{20}$	240	This Work
$\text{La}_{1-x}\text{Nd}_x\text{MgAl}_{11}\text{O}_{19}$	$3 \times 10^{19}$	360	5
	$3.4 \times 10^{20}$	260	5
	$1.1 \times 10^{21}$	52	5

in Table 2 indicate that the fluorescent lifetimes are quite long in the beta" alumina host, even at very large  $\text{Nd}^{3+}$  concentrations. This suggests that  $\text{Nd}^{3+}$  in the beta" alumina conduction plane is less susceptible to the self-quenching effects which cause serious reduction in lifetime and quantum efficiency at concentrations above  $1\%$  in YAG hosts. Additional optical studies are in progress.

## 4. Conclusions

Trivalent ion exchange in beta" alumina is a completely unexpected and extraordinary phenomenon. The trivalent beta" aluminas appear to be the first solid electrolytes to exhibit rapid trivalent cation motion, thus demonstrating that fast ion transport in solids extends beyond monovalent and divalent ions. In addition, these trivalent beta" aluminas possess interesting optical properties. These properties not only permit new structural information to be derived, but also suggest that the trivalent beta" aluminas may have potential optical applications.

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